PB82-167198

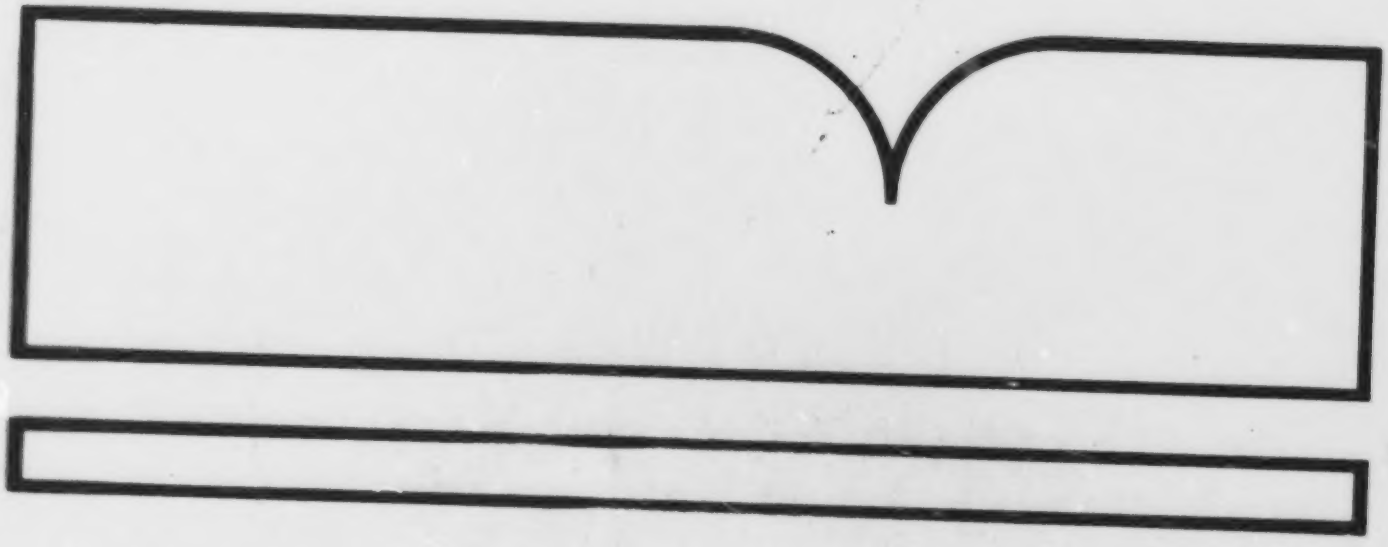
Critique of Methods to Measure Dry Deposition
Concise Summary of Workshop

Argonne National Lab., IL

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Jan 82



U.S. Department of Commerce
National Technical Information Service
NTIS.

PB82-167198

EPA-600/D-82-155
Book Article

CRITIQUE OF METHODS TO MEASURE DRY DEPOSITION
CONCISE SUMMARY OF WORKSHOP

by

Bruce B. Hicks* and Marvin L. Wesely
Argonne National Laboratory
Argonne, Illinois 60439

and

Jack L. Durham
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

*Present address: ATDL-NOAA
Oak Ridge, Tennessee 37830

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-82-155	2. Book Article
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE CRITIQUE OF METHODS TO MEASURE DRY DEPOSITION CONCISE SUMMARY OF WORKSHOP	5. REPORT DATE January 1982
	6. PERFORMING ORGANIZATION CODE 054134
7. AUTHOR(S) Bruce B. Hicks, M.L. Wesely and J.L. Durham*	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Argonne National Laboratory Argonne, Illinois 60439	10. PROGRAM ELEMENT NO. C1MH1E/01 FY80 0510 & CDTA1D/01 11. CONTRACT/GRANT NO. ~~FY81 1100~~ IAG 78-D-X0193
12. SPONSORING AGENCY NAME AND ADDRESS *Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

At the Workshop on Dry Deposition Methodology, held December 4 and 5, 1979, at the Argonne National Laboratory in Argonne, Illinois, dry deposition measurement techniques were assessed for routine monitoring use. A majority opinion was reached that commonly-used techniques such as surrogate surfaces and collection vessels are not sufficiently accurate for use in networks, because the highly varied properties of the natural surfaces of interest cannot be simulated adequately. Further research was recommended on dry deposition parameters in order to estimate dry deposition rates, if possible, from measurements of atmospheric concentrations at a single height, together with observations of surface properties and micrometeorological parameters. The ability to perform such investigations in the field is critically dependent upon advances in chemical and physical capabilities to provide methods with standard relative errors of less than 1 percent for a single instrument on successive measurements, or with time responses of less than 1 second. These requirements are not being achieved for many pollutant species. At present, the most promising methods for monitoring are eddy accumulation, modified Bowen ratio, and variance. Regardless of the method employed, monitoring sites should be chosen that are representative of the surrounding areas in terms of surface properties, meteorological conditions, and pollutant characteristics.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

INTRODUCTION

Within the last decade, there have been improvements in urban air quality, but deterioration has occurred on the regional scale. Contributing factors are the shifting of electrical power generation to rural areas and the use of tall stacks. There has been a recent awareness of the decline of visual quality in the eastern United States, and a serious concern for what now appears to be a significant trend of increasing quantities of strong acids removed from the atmosphere by both wet and dry deposition.

The subject of dry deposition addresses all processes by which airborne contaminants are removed from the atmosphere at the surface of the earth, excluding those processes directly aided by precipitation. Ultimately, knowledge of the fate of pollutants is desired, particularly if the effects are harmful. For surface vegetation, for example, dry deposition can sometimes be equated to a dose that causes specific harmful effects, but often the effects of pollutants on biological systems occur after transport away from the initial surface contacted and after some change in chemical form. Since the surface flux of atmospheric contaminants affects concentrations downwind, dry deposition affects the extent of areas in which significant concentrations of pollutants are found. Thus, dry deposition exerts a strong, indirect influence on concentrations of pollutants found in precipitation and on interactions between pollutants.

Of concern here is primarily the rate of removal by dry deposition of pollutants in the atmosphere, to some extent their immediate fate, and less their effects, except those that aid in determining deposition rate. Methods used to assess or predict rates of dry deposition are extremely diverse, largely because the types of contaminants and surfaces vary greatly. Since the final assessment of dry deposition must take place for the actual environment considered, relevant studies have concentrated on experimental efforts in the field. Laboratory and purely theoretical work play a necessary

role in understanding the processes that control dry deposition. Such understanding leads to a productive use of data from networks monitoring air quality, helps extrapolate present deposition results to pollutants not yet fully investigated, and leads to better parameterizations of surface removal for use in numerical models of pollutant distribution in the atmosphere. Presently, our knowledge of rates is too limited, and our ability to monitor in networks is severely restricted.

There has been a continuing interest in dry deposition for many years. Theory, methodology, and experimental results have been reviewed in an Energy Research and Development Agency symposium (1974)[1] and in many subsequent papers. However, it was not the intent of the U.S. EPA workshop on dry deposition (Dec 79)[2] to provide an updated summary of the status of this research field.

The purpose was: (1) To identify the advantages and disadvantages of current methods for measurement of dry deposition of air pollutants, (2) To speculate on the potential of other methods, and (3) To make recommendations to EPA for research and development in regard to (a) research methods, instruments, field measurements, and tests, and (b) methods for evaluating and monitoring dry deposition on a routine or semi-routine basis.

The purpose was not: (1) To certify the methods and results obtained by the participants or others, or to lobby for a favorite method, (2) To address ecological effects, (3) To address transport modeling, and (4) To obtain a consensus on everything.

In this chapter, we present a concise summary of the workshop's critique of methods, identification of research needs on processes, and the conclusions/recommendations. Not presented here, but contained in the complete workshop report, are: (1) brief descriptions, specific critiques, and recommendations for individual methods that were discussed at the workshop, (2) list of participants, and (3) the complete texts of the dissenting views.

CRITIQUE OF METHODS

This section presents brief descriptions and evaluations of various experimental methods for investigating and estimating dry deposition. The methods are representative of most research to date, and include some especially promising techniques. Purely theoretical efforts are not considered separately, but this practice is not meant to imply that such work is unimportant. In fact, all of the experimental methods are directed to some extent towards developing better theories on deposition; the parameterization studies to be considered are specifically concerned with theoretical and semi-empirical expressions of processes that affect deposition.

The main focus is on methods capable of determining dry-deposition rates of various pollutants either by measurement alone or by a combination of measurements with numerical simulations. The methods are sorted into three categories: (A) estimates of accumulation, (B) flux monitoring, and (C) flux parameterization. These distinctions are somewhat artificial; the categories only reflect the intent of the methods as they are currently reported in the scientific literature. A summary of the critiques is given in Table 1.

If the total accumulation of certain pollutants on a given area could be measured directly, the answers most desired might be found without further effort. This approach constitutes the first category, (A) estimates of accumulation. Periods of time ranging from months to years are usually considered; short-term variations cannot be identified. While areas ranging in size from the entire surface of the earth to individual roughness elements can be addressed in principle, a more practical size is that of individual watersheds characteristically from 1 to 100 km in horizontal dimension. The methods of estimating accumulation could potentially be used for routine monitoring, but the effort required would probably be too large.

Numerous attempts have been made to monitor dry deposition, i.e., to measure fluxes directly on a routine basis. These techniques usually involve sampling at

individual points; they are considered in the second category, (B) flux monitoring. Single measurements typically last from hours to weeks, and so shorter-term variations are usually not detected. Ideally, the point measurements are taken over a well-defined surface, e.g., one of uniform vegetation. Actually, all of the point- and areal-sampling field methods listed in Table 1 are potential monitoring techniques, but those listed in category B are the ones that to date have been used most often for monitoring.

The last, and largest, category of purpose to consider is (C) flux parameterization. Many of the field methods listed may become useful for routine monitoring as technology develops; at present, however, these methods in Category C, as opposed to those in Category B, are used primarily for understanding and parameterizing deposition processes. With successful parameterizations, concentrations measured directly or computed in numerical models can be utilized to calculate the vertical fluxes. Category C is further divided into two subcategories according to whether the work is performed in the field or in the laboratory. For field work, both large areas of 1 to 100 km in horizontal extent and small areas of uniform surface characteristics are considered. Sampling times vary from 10 minutes to several days. During short-term studies over small areas, great effort usually must be made to obtain sufficient information on the physical, chemical, and biological characteristics of the surface. For laboratory work, sampling periods are highly variable, but usually short. The type of laboratory observations considered here is concerned with bulk exchange processes in rather large enclosures.

TABLE 1. SUMMARY OF METHODS TO MEASURE DRY DEPOSITION
(Only those methods for particles that are not affected by gravitational settling are considered.)

Category	Method	Pollutant		Monitoring Potential	Research Potential
		Particles(P)	Gases(G)		
A. Estimates of Accumulation	Atmospheric radioactivity	P		low[a]	medium[b]
	Mass-balance studies	P	G	low[a]	high[c]
B. Flux Monitoring	Open pots	P		low[d]	low[b,d]
	Flat filters	P		low[d]	low[b,d]
	Flat plates and shallow pans	P		low[d]	low[b,d,q]
	Fiber filters	P		low[d]	low[b,d]
	Sticky films	P		low[d]	low[b,d]
C. Flux Parameterization					
1. Field work					
a. Large areas	Box-budget studies	P	G	low[a]	medium[e]
	Airborne eddy correlation	P	G	low[a]	high[f,g]
b. Small areas	Gradient	P	G	low[h]	high[i]
	Modified Bowen ratio	P	G	high	high[i,j,k]
	Eddy correlation	P	G	low[h]	high[f]
	Variance	P	G	high	high[f,i,j]
	Tracer experiments	P	G	low[a]	medium[l]
	Eddy accumulation	P	G	high	high[l]
	Leaf washing	P	G	medium[a]	medium[m]
	Surface snow sampling	P	G	medium[n]	medium[n]
2. Laboratory	Chamber studies		G	low	high[o]
	Wind-tunnel studies	P	G	low	high[p]

[a] large effort required
[b] poor particle size discrimination
[c] addresses fate of pollutants to some extend, does not discriminate between particles and gases
[d] easy to collect sample but difficult to interpret, contamination by gases possible
[e] difficult to achieve the absolute accuracies required
[f] requires fast-response instrumentation
[g] only pollutant tried so far has been ozone
[h] instrumentation difficult to maintain
[i] susceptible to contamination by resuspension of particles
[j] not yet tried for pollutants
[k] requires small short-term drift of sensors
[l] data difficult to interpret
[m] leaf-to-leaf variability is large
[n] works only for light winds, subfreezing temperatures
[o] used mostly to identify important processes
[p] levels of turbulence found in the field difficult to achieve realistically
[q] alternative viewpoint expressed

INDIRECT CALCULATION OF DEPOSITION RATES

Another method for determining deposition is always implied to some extent when parameterization is discussed. This more indirect method is the application of parameterizations to measurements of pollutant concentrations and a few selected companion variables in order to compute the dry deposition rates indirectly. The use of concentrations monitored at a network of stations is emphasized here, but concentrations computed by numerical models is inherently considered also.

For airborne particulate and gaseous pollutants, there is no historical data base on dry deposition except for some exceptional cases such as architectural surfaces. However, there are data bases on air quality and there are networks for measuring air quality in operation at the present time. Thus, an approach to monitoring dry deposition is to use the measurements of air-pollutant concentrations at a single height and employ parameterizations of dry deposition to yield the deposition rates. From micrometeorological observations and knowledge of surface behavior, deposition velocities are inferred. Pollutant flux is obtained as the product of deposition velocity and concentration. Companion variables that form the basis for the meteorological calculations are wind speed, atmospheric stability, and surface roughness; depending on pollutant and surface characteristics, a range of other properties must be monitored. This method has an advantage in that monitoring stations are already in place for some pollutants. Unfortunately, however, single-height concentration monitoring is fundamentally deficient. Meteorological information alone will not yield a measurement of deposition velocity because it cannot account for all surface variables, such as the physiology of vegetation. Thus, careful observations of surface characteristics must be made. While it is probably not essential that the concentrations be measured at extremely uniform sites, micrometeorological measurements should be. The alternative, less exact but more practical method is to infer atmospheric variables from standard meteorological measurements and assume diurnal cycles of stability.

Until reliable methods suitable for directly monitoring dry deposition are developed, use of monitored concentrations may be the only alternative that is practical yet sufficiently accurate. Parameterizations of SO_2 and O_3 fluxes to many surfaces are already available, but are not well founded for submicron particles and many gases. For surfaces, additional work above tall plant canopies such as forests is needed.

SOME RESEARCH NEEDS

An attempt is made here to describe some of the processes controlling dry deposition that need to be better understood, and to suggest methods of research that might be employed. These considerations complement the flux parameterization methods identified in Table 1. The major problem in parameterizing the flux of specified pollution species to a given surface can often be identified by noting where the resistance to vertical transport is greatest. For example, uptakes of certain gases by vegetation is mainly controlled by the sizes of the leaf stomatal openings. For submicron particles, deposition to smooth inert surfaces is limited by the slow diffusion through the quasi-laminar layer of air closest to the surface; any means of effectively short-circuiting that resistance can result in large changes in deposition rates.

Practical considerations limit the number of chemical species and types of surfaces that can be investigated. The surfaces chosen for study usually should be those most prevalent or characteristic of the area or region considered. At a minimum, the pollutants to be examined should be the criteria pollutants and particles in many small size intervals, with emphasis on submicron diameters. Of course, studies are aided by grouping together pollutants with similar chemical and physical properties. Categories might depend on solubility in water or reactivity with various substrates, for example. For particles, the processes of diffusion, impaction, and sedimentation can sometimes be studied separately, but care must be taken because these are smooth functions of particle size in overlapping size ranges.

Table 2 summarizes identified research needs, grouped according to scales of the phenomena of interest and correlated with experimental methods of investigation given in Table 1. The smallest scale sizes, those associated with r_e in Table 2, are often best studied in the laboratory, where, for example, reactivity with various substrates can be examined. Further work on particle deposition is needed to

TABLE 2. SUMMARY OF RESEARCH PRESENTLY NEEDED ON DRY DEPOSITION PROCESSES

Contributing Process (resistance)	Length, Scale or Height (m)	Topics of Concern	Recommended Methods of Experimental Research
r_e, resistance of individual surface elements	<<1	Particles: surface wetness, stickiness, microscale roughness, electrostatic attraction Gases: numerous chemical and biological factors as they interact with pollutants having various properties[a]	All with medium or high research potential identified in Table 1
r_ℓ, resistance of quasi-laminar layer enveloping surface elements	~0.005	Particle deposition as affected by impaction and diffusion[a]	Wind-tunnel studies plus all small-area field flux-parameterization techniques (C.1.b. in Table 1)
r_s, bulk surface resistance, composed mainly of r_e's and r_ℓ's	<30	Relationship of mean vertical aloft to transport to individual surface elements	Micrometeorological techniques[b] applied in conjunction with leaf washing, tracer studies, mass-balance studies, and similar methods
r_a, aerodynamic resistance in the atmospheric surface layer	~50, day ~ 5, night	Similarity theory applied to vertical gas transport[c]; Transport in very stable conditions[c]	All micrometeorological techniques[b]
r_a, and r_ℓ as affected by medium-scale surface discontinuities	<30	Increased aerodynamic roughness, Increased aeration of plant	Complex geometry[d]: box-budget studies, airborne eddy-correlation, atmospheric radioactivity, mass balance studies Simple geometry[d]: wind-tunnel studies, tracer studies
r_b, resistance in the planetary boundary layer	~1500, day ~ 100, night	Vertical flux divergences due to physical and chemical processes	Box-budget studies, airborne eddy correlation

[a]probably where initial research emphasis should be placed
[b]the gradient, modified Bowen-Ratio, eddy-correlation, variance, and eddy-accumulation methods
[c]not felt to be particularly important in research presently needed
[d]not specifically considered at the workshop

determine the effects of surface stickiness and microscale roughness. Continued work on diffusiophoresis, thermophoresis, and electrophoresis is needed, but with greater emphasis on the environmental conditions that exist in the field. For example, electrical charges on particles vary with the "age" of the aerosol, resulting in varying effects of electrophoresis on deposition. Another problem is that pollutants are often (re)suspended or (re)emitted, due to a variety of causes that are often not appreciated until what appears as anomolous results are found in laboratory and field experiments. Small-scale surface phenomena that need to be studied in this respect include decomposition of organic material and chemical reactions at surfaces that "recycle" pollutants.

Next to the actual surface is the quasi-laminar boundary layer with a resistance r_ℓ often considered separately. A considerable amount of wind-tunnel work has been performed on phenomena of this scale size. If possible, both laboratory and theoretical studies should consider the high levels of atmospheric turbulence and its effects on the interfacial air layer. For example, the intermittent penetration of strong gusts into deep plant canopies during unstable conditions strongly modifies both the concentration of certain pollutants and the thickness of the boundary layers of air around surface elements.

A difficult theoretical and experimental problem concerns the process by which transfer to surface elements is added up to yield the total deposition from the atmosphere. Micrometeorological techniques usually only yield an estimate of bulk surface resistance (r_s in Table 2) that may not be adequate by itself to identify the controlling process. For present purposes, the goal sought should be simple parameterizations of bulk surface and interfacial sublayer resistances or filtration efficiency. Both numerical and analytical models have been attempted; they usually rely to some extent on empirical relationships found in laboratory and field work. A by-product of such models is the calculation of the accumulation of harmful pollutants to parts of the surface.

On the largest scale sizes, those concerning r_a and r_b in Table 2, application of the parameterizations gives deposition velocities for uniform surfaces; the deposition rates for large diverse areas are computed as an average of contributions from each surface weighted in proportion to the total area covered by each surface. Several sources of error can affect the estimates. For example, the fluxes themselves alter the concentrations, so that use of a single concentration for many types of surfaces is inaccurate. Also, the effects of surface discontinuities may result in altered deposition rates near boundaries of an area with a single type of surface. Obstacles such as trees and isolated buildings have an effect, not to mention the unknown extent to which complex terrain can alter the parameterizations. Obviously, experimental and theoretical methods used to assess these effects should be developed further. Perhaps box-budget experiments can be used to determine errors; such procedures may in the future be sensitive enough to detect the large errors that are of greatest concern.

CONCLUSIONS AND RECOMMENDATIONS

The rate of dry deposition of atmospheric pollutants depends on many factors concerning the pollutants, surfaces, and atmospheric conditions. To evaluate methods that might potentially be used to monitor dry deposition, the roles of all contributing processes must be considered, at least in broad categories. The most important processes that affect deposition rates can often be identified as those corresponding to the largest resistance to vertical transport or uptake.

For small particles that are deposited by diffusion and impaction, deposition is strongly affected by the resistance of the quasi-laminar sublayer of air nearest to surface elements and by the microscale roughness and stickiness of the surface. For gaseous pollutants, the chemical and biological nature of a surface, as well as its physical configuration, often dominates the resistance to air-surface exchange. Processes of (re)emission and (re)suspension, which can greatly affect net deposition, are also highly dependent on surface properties. Hence, the following recommendation can be made:

1. Since use of artificial collecting surfaces does not simulate the net dry deposition of particles and gases to natural surfaces, it would be ill-advised to rely upon continued monitoring by "open pot" or various other types of surrogate surfaces. As a result, present capabilities to monitor dry deposition in a practical, yet accurate, manner are inadequate.

Use of such surfaces has continued for estimating deposition of particles in some cases, simply because of the lack of better procedures that can be utilized with small cost and effort. Notably, knowledge on how to "calibrate" surrogate surfaces for gaseous or particulate deposition will probably never be obtained. At best, future efforts might relate the amount and type of material collected by a surrogate surface to a corresponding atmospheric concentration; it would then remain necessary to deduce surface fluxes from the inferred concentrations, not an easy task in most cases

at present. It would probably be easier and more accurate over natural surfaces to measure concentrations directly rather than relying on artificial surfaces intended to simulate the actual surface.

In the process of choosing a site for monitoring (which assumes that a suitable monitoring technique is available), the importance of knowledge of surface characteristics must be emphasized. This consideration is reflected in another recommendation:

2. Sites chosen for monitoring should have a surface "typical" of the surrounding area; in the immediate vicinity of measurements, the surface should be a single uniform type. The condition of local vegetation and the general environmental conditions that affect the surface should be recorded.

Obviously, there might be some difficulty in finding suitable sites in many locations. An additional requirement for site selection is:

3. Monitoring sites should have pollutant and wind characteristics representative of the large surrounding area. Records should be maintained on the possible presence of pollutants from local sources and on local meteorological events such as precipitation, fog, and dewfall.

The above two requirements for a good site imply that sites currently chosen for wet and dry deposition monitoring may not be adequate for obtaining representative estimates of dry deposition.

For monitoring, estimates of atmospheric resistance should be made routinely, since this resistance can control the transfer of pollutants that can be removed very efficiently by the surface, and since it is important to identify conditions of atmospheric decoupling at night, when turbulent vertical transport becomes exceedingly small. Provided a few essential measurements of atmospheric conditions are taken, micrometeorological formulations currently available are adequate for estimating the atmospheric resistance to vertical transport from a height of several meters to fairly close to the surface. It is recommended that:

4. At each monitoring site, wind speed, atmospheric stability, and aerodynamic surface roughness should be determined, so that atmospheric resistances can be calculated and averaged over time intervals preferably not to exceed six hours; one-half to one hour is optimum.

Current techniques intended to monitor dry deposition directly on a routine basis do not appear to be adequate. As stated above, surrogate collecting surfaces do not simulate surface conditions sufficiently well in most cases. An alternative method is to attempt to infer surface fluxes from pollutant concentrations measured at a single height; much work has already been devoted to develop the technical means to perform the needed measurements. Concentration measurements at one height, however, give no information on transfer processes in the atmosphere and at the air-surface interface. The following recommendation must therefore be made:

5a. Concentration measurement at a single height should not be used by itself to provide a measure of dry deposition.

The availability of measurements of some pollutant concentrations leads to questions as to what supporting information is required in order to interpret these measurements. Deposition rates can be estimated as the product of concentration and an appropriate deposition velocity. The latter quantity can be derived from accurate parameterizations of the deposition processes. As implied in Recommendation 4 above, micrometeorological aspects of parameterizations can be estimated fairly well above uniform sites. However, interactions of pollutants with the surfaces and the behavior of small particles in the interfacial air layers are not well understood. Therefore, to interpret past and future measurements on concentrations, at least until means sufficient for accurately and routinely monitoring dry deposition are developed, further research is needed. The following statement concludes Recommendation 5:

5b. In order to understand the relationships between vertical fluxes and concentrations measured at a single point, research on the parameteriza-

tion of deposition processes should continue by use of a variety of theoretical approaches and experimental techniques in the laboratory and the field.

Cooperative efforts between micrometeorologists, biologists, and aerosol scientists, among others, are required; many recent studies have not utilized such cooperation. For example, atmospheric investigations often do not study a minimum set of variables concerning pollutant and surface characteristics in order to elucidate the deposition processes. On the other hand, ecological studies often do not adequately document atmospheric conditions.

Based on present knowledge, it is possible to identify certain information that would need to be obtained routinely at monitoring sites in order to estimate deposition velocities for evaluating surface fluxes from concentrations measured at a single height. Of course, this needed information must also be obtained during the parameterization studies that form the basis for this possible monitoring technique. As already stated, wind speed at some specified height above the surface should be measured and atmospheric stability estimated, both for periods not to exceed six hours. The type, height, and condition of vegetation present should be known. Furthermore, consideration should be given to a number of other factors that appear to be important in the case of certain pollutant species. Soil moisture content can affect the uptake of some gaseous pollutants, especially over bare soil. Some measure of aridity and atmospheric stability might suffice to describe the gross aspects of physical environment that affect plant physiological functions; relative humidity and solar radiation measurements might suit this purpose. Other variables, particularly those dealing with conditions of vegetation, will probably be identified as important yet suitable for routine evaluation, as a result of future parameterization studies.

Deposition velocities depend on the type of pollutant as well as on surface and atmospheric conditions. For particles, studies have indicated that deposition is

affected by diffusion, impaction, and sedimentation processes that are continuous functions of particle size in overlapping ranges. Measurements employing a single size fractionation of particles (and hence providing samples of "large" and "small" particles) are not satisfactory, since it is likely that the course and fine fractions each must be resolved into several size classes. Gases can be considered in categories of similar chemical properties only to a limited extent. Thus, to infer dry deposition from measurements of concentration at a single height, direct measurement of each pollutant of interest is required. The possible importance of (re)suspension and (re)emission processes further underlies this need.

To perform parameterization research such as implied in Recommendation 5b, one would surmise that there are or will be available methods to measure reliably the deposition rates. In that case, the measurement techniques might themselves offer the best means to monitor deposition rates. The corresponding recommendation is:

6. Techniques used in field parameterization studies should be developed and examined for applicability to routine monitoring.

The methods most recommended are micrometeorological in nature. Verification of the techniques requires some direct measurements of accumulation at the surface; box-budget experiments, though usually too inaccurate, may someday provide an estimate of errors. The following statement, at least, can be made:

7. Although micrometeorological methods offer the promise of providing a direct and precise measure of dry deposition, experimental complexity and sensor inadequacies combine to reduce confidence in them. At this time, no micrometeorological method can be accepted with absolute confidence. There is need for continued intercomparison and comparison with other methods.

Fluxes of particles large enough to be affected significantly by gravitational settling cannot be measured accurately by standard micrometeorological techniques. In fact,

if such large particles are not excluded from detection in some techniques, erroneous results might be obtained.

Some micrometeorological methods can be identified as possibly worthy for development for use in monitoring. They are the variance method, the eddy-accumulation techniques, and the modified Bowen-ratio technique. Others may be indicated as research progresses. For the variance methods, the main limitation seems to be in the ability to find or develop chemical sensors that have fast response (at least 1 Hz) in addition to being linear and having low noise. The other two methods, and others likely to be suggested, rely on accurate mean measurements of concentration differences. Therefore, the following recommendation is made:

8. Methods to measure dry deposition that depend on concentration differences detected in samples collected in the atmosphere must be supported by chemcial/physical analysis methods with standard errors of 1% or less.

This recommendation does not necessarily imply that absolute accuracies must be 1% or less. The modified Bowen-ratio technique is used, for example, a single sensor might be rigged to alternately measure at two heights. Then the requirement is that the difference, which will usually be 1 to 10% of the mean, be measured accurately. Thus sensor offsets and slow drifts have almost no effect, and errors, say of >10%, in span calibrations would produce errors of only >10% in the estimated vertical flux.

Techniques to measure, let alone monitor, fluxes of species associated with acid deposition are presently deficient. Many of the reasons have already been given in this section. There is an urgent need to develop methods with the required accuracy in measuring amounts of strong acids and species such as H_2SO_4, HNO_3, $SO_4^=$, NO_3^-, NH_4^+, NH_3, and organic acids and bases. This need leads to the following recommendation:

9. Present capabilities to measure dry deposition for parameterization studies as well as for monitoring must be improved in order to support the acid deposition programs of EPA.

DISSENTING VIEWS

Potential of Micrometeorological Methods

Dry deposition measurement methodology is a combination of two disciplines: (1) the micrometeorological measurement or inference of air transport parameters and (2) quantitative chemical analysis. The workshop has critiqued various methods mainly from the viewpoint of physical mass transport parameters, which is expected since most of the workshop participants were micrometeorologists. The degree of accuracy of chemical analysis is stated for several of the techniques; however, the unreasonable difficulty of such demands on the chemical analyst is not discussed. Not demonstrated is the requirement of non-surrogate surface dry deposition measurement procedures to be able (a) to detect mean concentration differences of 1 to 10% in successive samples to within an accuracy of 10%, or (b) to monitor pollutant air concentrations with a response time of one second or less. However, if such requirements are valid, the successful achievement of chemical/physical measurements in a routine monitoring network is an unreasonable expectation. In general the error in flowrate measurement for aspirated samples is not better than ±10%. If this fluctuation error could be reduced to ±1% (which is unlikely), the chemical measurement random errors are expected to be too large to be acceptable.

The extreme requirements for precision/response time of the chemical analysis/monitor make it unlikely that such methods will be developed rapidly, as evidenced by the total absence of even one routine dry deposition monitor based on eddy accumulation, modified Bowen-ratio, or variance techniques.

Sample Integrity

While a legitimate need may exist to monitor the "dry deposition of pollutants, especially the strong mineral acids," known atmospheric chemical behavior is ignored in regard to the preservation of sample integrity. For example, the presence of strong mineral acids in fine aerosols has been demonstrated; however, the presence of such

acids in a dry deposition sample (from a bucket, plate, or filter collector) is highly improbable because eventual neutralization by ambient ammonia will occur over the collection period (several days). Of at least equal importance is the simultaneous collection of large mineral particles that are bases, which neutralize the acids during extraction. Our previous experience has been that dust-fall bucket samples invariably yield a basic aqueous extract. Such a result is contrary to the suspected acidification of surface waters in the northeast.

Use of Surrogate Surfaces

Surrogate surface deposition measurements of various types have been conducted for years, and will probably continue to be used on a widespread basis. Simplicity in obtaining the data, control over contamination, ability to collect sufficient material for trace level analysis, and low expenses are the primary reasons. It is acknowledged that certain applications of such measurements in particular may not provide as much accuracy as more sophisticated techniques, however sufficient data are not available to establish conclusively that all types of surrogate surfaces should not be used.

Several surrogate surface studies reported in the literature have shown consistencies in the data which suggest that semi-quantitative information can be obtained. (The results of eight separate investigations are cited in the workshop report.[2])

Recommended research includes determination of the relationships among material suspended in the atmosphere, collected by surrogate surfaces, and deposited on natural surface elements (as determined by washing and microscopic examination, or other techniques). Such comparison studies might lead to a better design and application of certain artificial surfaces than those routinely used for monitoring, such as the use of flat plates situated in the foliar canopy as opposed to the use of buckets at ground level.

SUMMARY

The workshop report[2] provides evaluations of various methods for estimating dry deposition of gaseous and particulate pollutants from the atmosphere to the surface of the earth. The intent is to provide the scientific information needed in order that sound decisions can be made on research, development, and coordination with regard to dry deposition. Existing and potential techniques for monitoring and parameterizing dry deposition are considered systematically and specific recommendations are given for each method on its present and potential usefulness. The viewpoints presented are based on and limited to opinions expressed during discussion that took place at the workshop. A priority of research needs was not established at the workshop and thus is not given here.

The current capabilities for monitoring dry deposition are felt to be inadequate because the methods now used, which usually employ surrogate surfaces or open vessels, do not give the deposition at the actual natural surface. Most of the workshop participants felt that "calibration" of such methods would not be successful or have very limited success. However, 20 to 30% of the scientists present who have been or are making original contributions to scientific research on dry deposition feel that the use of surrogate surfaces should be pursued in some fashion.

Fairly direct measurements of the net dry deposition can be obtained by measurement of the accumulation of certain chemicals in rather large areas over long periods of time. Because of the considerable amounts of effort necessary in application, this category of method clearly was never intended to apply to routine monitoring, although the results of such studies are quite useful in determining the fate of pollutants after reaching the surface.

Parameterization studies are directed toward understanding the relationships between vertical fluxes and the properties of pollutants, surfaces, and the atmosphere. Estimation of deposition rates needed for numerical simulations of pollutant behavior

in the lower atmosphere usually are based on parameterizations of the deposition velocity (the ratio of flux to concentration at a specified height in the atmosphere). In the report, evaluations of numerous methods are presented. Of course, knowledge accumulated from parameterization studies might allow the use of pollutant concentrations monitored at a single height to estimate the vertical flux. To date, very few species of pollutants have been studied adequately to approach this goal. For example, the behavior of many species associated with strong acids has not been determined, because the chemical sensors presently available do not meet the specifications required by the techniques for measuring dry deposition. In many cases, there is no "sensor" but instead a procedure for chemical analysis best performed in a well-equipped laboratory. Usually, measurement procedures should be able to detect mean differences of 1 to 10% in successive samples to within an accuracy of 10%, in order to be useful to measure deposition rates. For flux measurement techniques that rely on detection of turbulent fluctuations in pollutant concentrations near the ground, the speed of response should be one second or less.

A simple, but accurate, method for monitoring dry deposition rates routinely is not available. Micrometeorological methods that have potential in this regard are the techniques of eddy accumulation, modified Bowen-ratio, and variance methods. It should be remembered, though, that even if these or other methods prove very useful, the requirements on the selectivity and performance of chemical and physical sensors are still quite high and, in many cases, not yet achievable.

Sites selected for parameterization and monitoring studies ideally should be located in uniform terrain so that results are not affected by unusual features of the surface unique to that location. Monitoring sites, if they are to be effective, should be located at surfaces that are typical of the surrounding areas and that should have representative meteorological conditions and pollutant characteristics.

ACKNOWLEDGMENT

The U.S. Environmental Protection Agency thanks the workshop participants for their contributions and Argonne National Laboratory, Argonne, IL, for hosting the meeting.

REFERENCES

1. "Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974)," Symposium Proceedings, Richland, WA, 4-6 Sep 74. U.S. Energy Research and Development Administration Report No. CONF-740921 (1976). Available from NTIS.

2. Hicks, B.B., M.L. Wesely, and J.L. Durham. "Critique of Methods to Measure Dry Deposition," U.S. EPA Report EPA-600/9-80-050 (1980). Available from NTIS (No. PB81 126443).